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(54) Title of Invention: Thin-film EL element

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Specification1. Title of Invention

Thin-film EL element.

2. Patent Claims

(1) Thin-film EL element, characterised in that a rare earth complex represented by the formula:



is used as the luminescent material.

In the formula,

R_1 and R_2 each independently mean a 1-15 carbon alkyl group, halogenated 1-15 carbon alkyl group, 6-14 carbon atom aryl group, or a 5- or 6-membered heterocyclic group containing one hetero atom;

R_3 means a hydrogen atom or the same as the group R_1 ;

and Z is a moiety represented by

① M (where M means a rare earth element),

- ② MA₂ (where A is a phosphine oxide, and M has the same meaning as aforesaid), or
- ③ MB (where B is a phenanthroline, and M has the same meaning as aforesaid).

(2) Thin-film EL element according to Claim 1, characterised in that the luminescent material is placed between two electrodes, and a base plate is provided on the outside of one of these electrodes.

3. Detailed Description of Invention

Field of Industrial Application

The present invention concerns a thin-film EL (electroluminescent) element, with which light emission of high luminance and vivid colour is obtained with a low applied voltage.

Prior Technology and Problem to be Solved

EL elements have the characteristics that their visibility is high because of self-luminescence, moreover their impact resistance is excellent since they are completely solid elements, and at present EL elements using ZnS : Mn, which is an inorganic phosphor, are widely used. However, since such inorganic EL elements require an applied voltage in the region of 200 V in order to luminesce, the drive systems are complex.

On the other hand, because the applied voltage can be substantially reduced, organic thin-film EL elements that use various materials are being developed. Previously, Vinsett et al. made an EL element using a thin film with a film thickness of ca. 0.6 μm with atracene [sic] as the emitter, and obtained clear blue visible luminescence with an applied voltage of 30 V (Thin Solid Films, 94 (1982) 171). However, there are problems in that the luminance of this element is inadequate; also a high applied voltage is still required.

Further, in recent years, organic EL elements which show luminescence with a luminance of 5-90 cd/m^2 simply on application of a low voltage of ca. 10 V have been made in thin films using the LB method (Langmuir-Blodgett method) (for example Iaid-Open Japanese Patent 61-43682). However with these organic EL elements, because the laminated film of electron-accepting and electron-donating luminescent substances is made by the accumulation of single molecule layers by the LB method, there are problems in that the structure is complex, and also they are complicated to produce, hence they are of little practical use.

Further, organic EL elements which display high luminance on application of low voltages of 25 V or less have also been developed (for example Laid-Open Japanese Patent 59-194393). These EL elements are a laminated type of the form electrode / hole injection layer / luminescent layer / electrode, and it is necessary for the film thickness between the electrodes to be 1 μm or less, and because of this there are major problems in that pinholes readily form, so that productivity is low.

Apart from the various aforesaid problems, there was a problem common to all of the previous organic thin-film EL elements mentioned above, in that the saturation was inferior. That is to say, because the emission spectrum width of the above-mentioned organic thin-film EL elements was broad, there were problems in that the colour vividness was inferior, and they poorly displayed the 3 single primary colours blue, green and red.

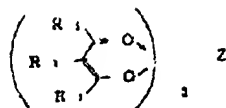
Also, organic EL elements with which luminescence of sufficiently high luminance is obtained at low voltages have been developed wherein the luminescent layer has a double structure, and a rare earth complex or the like is used as the luminescent organic compound (for example Laid-Open Japanese Patent 61-37887). However, the rare earth complexes indicated in this are just one part of this, and furthermore there was no disclosure whatever concerning improvements with regard to the luminance of the colours, in other words the vividness of the colours, emitted by the EL elements in which these rare earth complexes were in part used as the luminescent material.

The present invention was made in the light of the aforesaid situation, and its purpose is to provide a thin-film EL electrode which displays high luminance and a sharp spectrum and emits vivid colours, on application of a low voltage.

Means of Solving Problems

The present inventors, as a result of continued diligent research in order to achieve the aforesaid purpose, discovered that if a certain type of rare earth complex is used as the luminescent material, it has a large effect on the saturation of the colour emitted by the thin-film EL element, and thus arrived at the present invention. That is to say, the thin-film EL elements of the present invention have a structure wherein a rare earth complex represented by the formula:

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is used as the luminescent material.

Now, in the aforesaid formula,

R_1 and R_2 each independently mean a 1-15 carbon alkyl group, halogenated 1-15 carbon alkyl group, 6-14 carbon atom aryl group, or a 5- or 6-membered heterocyclic group containing one hetero atom;

R_3 means a hydrogen atom or the same as the group R_1 ;

and Z is a moiety represented by

- ① M (where M means a rare earth element),
- ② MA_2 (where A is a phosphine oxide, and M has the same meaning as aforesaid), or
- ③ MB (where B is a phenanthroline, and M has the same meaning as aforesaid).

Also, the thin-film EL elements of the present invention are preferably structured in such a way that the aforesaid luminescent material is placed between two electrodes, and a base plate is provided on the outside of one of these electrodes.

Below, the present invention's solution is described in detail.

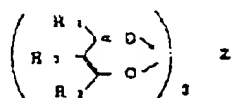
In the thin-film EL elements of the present invention, either an AC (alternating current) driver type or a DC (direct current) driver type can be used, but the following description relates to the DC driver type, and refers to Fig. 1.

In Fig. 1, 1 is a base plate, and is made of glass, plastic or quartz, or the like. 2 and 3 are electrodes between which the luminescent layer 4 is placed, and of these, one electrode 2 is formed on top of the base plate 1, and is made as a transparent or semi-transparent electrode using ITO (indium tin oxide), SnO_2 (stannic oxide), ZnO (zinc oxide) or the like. This electrode 2 is usually of thickness 50 nm - 1 μ m, and for the sake of transparency preferably 50-150 nm. Further, the other electrode 3 functions as the back (facing) electrode, and metals such as gold, aluminium, magnesium or indium are used. The film thickness of this back electrode 3 is usually 50-200 nm.

Now, depending on the type of thin-film EI. electrode, it is also possible to make the electrode 2 next to the base plate 1 the metal back electrode, and to make the other electrode 3 a transparent or semi-transparent electrode.

Depending on the luminescent material made up of a certain type of rare earth complex, the luminescent layer 4 is made in a film thickness of 100 nm - 5 μ m.

As this luminescent material rare earth complex, substances represented by the formula



are used.

In this,

R_1 and R_2 each independently is a 1-15 carbon alkyl group, such as for example a methyl group, ethyl group, propyl group, butyl group, i-propyl group, t-butyl group, i-butyl group, s-butyl group, octyl group or nonyl group;

a halogenated 1-15 carbon alkyl group (where halogen is chlorine, fluorine, bromine, etc.), such as for example a trifluoromethyl group, heptafluoropropyl group, trichloromethyl group, tribromomethyl [sic] group, dichloromethyl group, chloromethyl group, difluoromethyl group, fluoromethyl group, dibromomethyl group or bromomethyl group;

a 6-14 carbon atom aryl group, such as for example a phenyl group, naphthyl group, tolyl group, xylyl group or anthryl group;

or a 5- or 6-membered heterocyclic group containing one hetero atom, for example nitrogen, oxygen or sulphur, such as for example a pyrrolyl group, furyl group, thienyl group or pyridyl group;

R_3 means a hydrogen atom or the same as the group R_1 ;

moreover, the moiety Z:

firstly is represented as M,

where M is a rare earth element, such as Ce (cerium), Tb (terbium), Sm (samarium), Eu (europium), Ho (holmium), Pr (praseodymium), Gd (gadolinium [sic]), Er (erbium) or Tm (thulium),

and as a rare earth complex in this case, for example $[\text{Eu}(\text{BFA})_3]$, which is made up of Eu and BFA (benzoyltrifluoroacetone), is mentioned, and its structural formula is as follows:

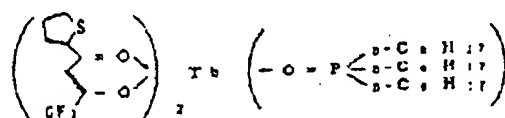
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secondly it is represented as MA_2 ,

where A is a phosphine oxide, for example a trialkylphosphine oxide, and may contain 6-12 carbon atoms in its alkyl part, for example it may contain n-octyl groups (8 carbons), and M has the same meaning as the aforesaid M,

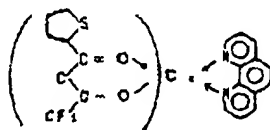
and as a rare earth complex in this case, for example $[Tb(ITA)_3(TOPO)_2]$, which is made up of Tb and TTA (thenoyltrifluoroacetone) and TOPO (tri-n-octylphosphine oxide) is mentioned, and its structural formula is as follows:



and thirdly it is represented as MB

where B is a phenanthroline, and M has the same meaning as aforesaid,

and as rare earth complexes in this case, $[Eu(TTA)_3(Phen)]$, which is made up of Eu and TTA and Phen (phenanthroline), $[Sm(NTFA)_3(Phen)]$, which is made up of Sm and NTFA (2-naphthyltrifluoroacetone) and Phen, and $[Ce(TTA)_3(Phen)]$, which is made up of Ce and TTA and Phen, and the like, are mentioned, and the structural formula of $[Ce(TTA)_3(Phen)]$ is as follows:



Concrete examples of the aforesaid rare earth complexes can be represented by (1-1) to (6-6) below:

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[formulae at foot of page 4 and all of page 5 to be inserted here]

Where M represents a rare earth element, and in the aforesaid (1-1) to (6-6), 1,10-phenanthroline or trioctylphosphine oxide can also be added.

The thin-film EL elements comprising structures such as the aforesaid are made by a process such as the following.

Firstly, a transparent electrode 2 is formed as a thin film on top of a base plate 1 for example by the vapour deposition method or sputter method. Next, a luminescent layer 4 is formed by creating a thin film of luminescent material on the upper face of this transparent electrode 2. This creation of the thin film is effected for example by the spin-coating method, casting method, LB method or vapour deposition method, and in terms of film uniformity, removal of pinholes, and the like, the vapour deposition is preferably effected under the following vapour deposition conditions:

Vapour Deposition Conditions

Boat heating conditions:	50 - 300°C
Vacuum:	10^{-5} - 10^{-3} Pa
Vapour deposition rate:	0.1 - 50 nm/sec
Base plate temperature:	-50 - 200°C
Film thickness:	100 nm - 5 μ m

After this, the back electrode 3 is formed as a thin film on the upper face of the luminescent layer 4, for example by the vapour deposition method or the sputter method.

Practical Examples

Practical Example 1

A transparent supporting base plate was made by preparing an ITO film of 50 nm thickness on top of a 25 mm x 75 mm x 1.1 mm glass base plate by the vapour deposition method, this supporting base plate was fixed in the base plate holder of a vacuum vapour deposition device (Nippon Vacuum Technology Co.), 200 mg of [Eu(BFA)₃] complex were placed in a resistance-heated molybdenum boat and the vacuum tank pressure was reduced to 1×10^{-4} Pa. Here, the [Eu(BFA)₃] was synthesised by adding a cyclohexane solution of BFA to an aqueous solution of Eu nitrate at pH 4.5. Since [Eu(BFA)₃] has the property that it migrates from aqueous solution to cyclohexane solution, it can be extracted by this means. After

extraction, the $[\text{Eu}(\text{BFA})_3]$ was obtained by removing the solvent under reduced pressure, and it was then purified.

Then the aforesaid boat was heated to 110°C , and a thin film of emitter of $1.5\ \mu\text{m}$ film thickness was obtained at a vapour deposition rate of $1.0\ \text{nm/sec}$.

Next, this was taken out of the vacuum tank, a stainless steel mask was installed on top of the thin film of emitter, it was again fixed in the base plate holder, 20 mg of gold were placed in the resistance-heated molybdenum boat and the vacuum tank pressure reduced to $1 \times 10^{-4}\ \text{Pa}$. After this, the boat was heated to 400°C , a gold electrode of 100 nm thickness was formed on top of thin film, and this was used as the facing electrode.

When a direct current voltage of 30 V was applied to this element, using the gold electrode as the positive electrode and the ITO electrode as the negative electrode, a current of 10 mA flowed, and a red luminescence was obtained. The maximum emitted wavelength during this was 618 nm, and the emission luminance was $80\ \text{cd/m}^2$. The CIE chromaticity coordinates were $x = 0.65$, $y = 0.34$, and it was a vivid red colour.

Practical Example 2

200 mg of $[\text{Tb}(\text{TTA})_3(\text{TOPO})_2]$ complex were placed in a heated boat similar to that in Practical Example 1, and the vacuum tank pressure was reduced to $1 \times 10^{-4}\ \text{Pa}$. For the $[\text{Tb}(\text{TTA})_3(\text{TOPO})_2]$ here, an aqueous solution of Tb chloride was adjusted to pH 4.5, a hexane solution of 2×10^{-4} moles of TOPO and 5×10^{-4} moles of TTA was added to this and mixed, and an extraction was then performed. Next, the $[\text{Tb}(\text{TTA})_3(\text{TOPO})_2]$ was obtained by removing the solvent under reduced pressure, and it was then purified.

Then the aforesaid boat was heated to 140°C , and a thin film of emitter of $1.2\ \mu\text{m}$ film thickness was obtained at a vapour deposition rate of $1.0\ \text{nm/sec}$. The base plate temperature during this was room temperature. Next, the element was made by forming a gold facing electrode in the same way as in Practical Example 1.

When a direct current voltage of 20 V was applied to this element, a current of 1.5 mA flowed, and a yellow-green luminescence was obtained. The maximum emitted wavelength

during this was 545 nm, and the emission luminance was 760 cd/m². The CIE chromaticity coordinates were $x = 0.34$, $y = 0.56$, and it was a vivid yellow-green colour.

Practical Example 3

200 mg of [Eu(TTA)₃(Phen)] complex were placed in a heated boat similar to that in Practical Example 1, and the vacuum tank pressure was reduced to 1×10^{-4} Pa. For the [Eu(TTA)₃(Phen)] here, an aqueous solution of Eu chloride was adjusted to pH 5.5, a solution of Phen dissolved in a 1:1 mixture of acetone and benzene was mixed with this, and an extraction was performed. Next, the [Eu(TTA)₃(Phen)] was obtained by removing the solvent under reduced pressure, and it was then purified.

Then the aforesaid boat was heated to 140°C, and a thin film of emitter of ca. 1.2 µm film thickness was obtained by vapour deposition of the [Eu(TTA)₃(Phen)] complex onto the transparent support base plate at a vapour deposition rate of 1.0 nm/sec. The base plate temperature during this was room temperature. Next, the element was made by forming a gold facing electrode in the same way as in Practical Example 1.

When a direct current voltage of 30 V was applied to this element, a current of 2.4 mA flowed, and a red luminescence was obtained. The maximum emitted wavelength during this was 618 nm, and the emission luminance was 280 cd/m². The CIE chromaticity coordinates were $x = 0.65$, $y = 0.34$, and it was a vivid red colour.

Practical Example 4

200 mg of [Sm(NTFA)₃(Phen)] complex were placed in a heated boat similar to that in Practical Example 1, and the vacuum tank pressure was reduced to 1×10^{-4} Pa. For the [Sm(NTFA)₃(Phen)] here, an aqueous solution of Sm chloride was adjusted to pH 5.5, a cyclohexane solution of Phen was mixed with this, and an extraction was performed. Next, the [Sm(NTFA)₃(Phen)] was obtained by removing the solvent under reduced pressure, and it was then purified.

Then the aforesaid boat was heated to 160°C, and a thin film of emitter of 1.1 µm film thickness was obtained at a vapour deposition rate of 1.0 nm/sec. The base plate temperature during this was room temperature. Next, the element was made by forming a gold facing electrode in the same way as in Practical Example 1.

When a direct current voltage of 40 V was applied to this element, a current of 37 mA flowed, and a red luminescence was obtained. The maximum emitted wavelength during this was 654 nm, and the emission luminance was 170 cd/m^2 . As a result, the CIE chromaticity coordinates were $x = 0.66$, $y = 0.32$, and it was a vivid red colour.

Practical Example 5

200 mg of $[\text{Ce}(\text{TTA})_3(\text{Phen})]$ complex were placed in a heated boat similar to that in Practical Example 1, and the vacuum tank pressure was reduced to $1 \times 10^{-4} \text{ Pa}$. For the $[\text{Ce}(\text{TTA})_3(\text{Phen})]$ here, an aqueous solution of Ce chloride was adjusted to pH 4.5, a solution of Phen dissolved in a 1:1 mixture of acetone and benzene was mixed with this, and an extraction was performed. Next, the $[\text{Ce}(\text{TTA})_3(\text{Phen})]$ was obtained by removing the solvent under reduced pressure, and it was then purified.

Then the aforesaid boat was heated to 145°C , and a thin film of emitter of $1.3 \mu\text{m}$ film thickness was obtained at a vapour deposition rate of 1.0 nm/sec . The base plate temperature during this was room temperature. Next, the element was made by forming a gold facing electrode in the same way as in Practical Example 1.

When a direct current voltage of 50 V was applied to this element, a current of 58 mA flowed, and a blue-violet luminescence was obtained. The maximum emitted wavelength during this was 400 nm, and the emission luminance was 89 cd/m^2 . The CIE chromaticity coordinates were $x = 0.17$, $y = 0.02$, and it was a vivid blue-violet colour.

From the aforesaid results, it was judged that by means of the thin-film EL elements of the present invention, the 3 primary colours red, blue and green are emitted with good saturation at high luminance and with a sharp spectrum, simply on application of a low voltage. Hence it became possible for example to create colour displays made up of thin-film EL elements which vividly show the different colours. Further, production of the thin-film EL elements is also simple, and it was judged that improvements in productivity can also be anticipated.

Effect of Invention

Hence the present invention has the effect that by means of its thin-film EL elements, the emission of vivid colours at high luminance is possible simply by applying a low voltage.

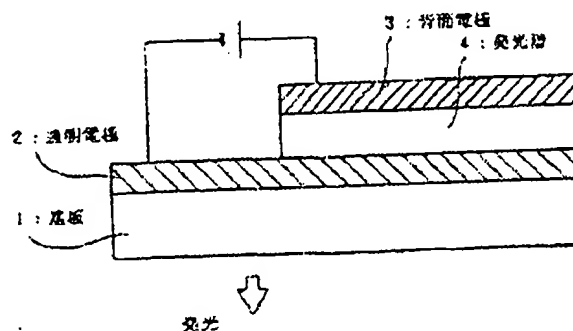
4. Brief Description of Diagram

Figure 1 is a simplified structural diagram showing one practical example of a DC driven form of the thin-film EL elements of the present invention.

- 1: base plate 2: transparent electrode
3: back electrode 4: luminescent layer

[By arrow: emitted light]

Fig. 1



Applicant: Idemitsu Kosan K.K.

Agent: Patent Attorney Watanabe Kihei

Formal Amendment

16 April 1988

To the Head of the Patent Office Mr Kunio Ogawa

1. Case Reference:

Patent application dated 7 April 1988.

2. Title of Invention:

Thin-film EL element.

3. Person Making Amendment:

Connection with case: Patent applicant

Address: Tokyo-to, Chiyoda-ku, Marunouchi 3-1-1

Name: Idemitsu Kosan K.K.

4. Agent:

Address: Tokyo-to, Minato-ku, Shinbashi 5-21-1, 3rd Shinto Building

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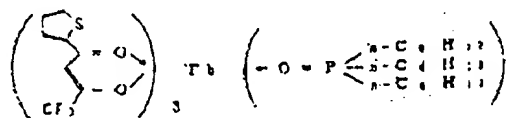
Name: Patent Attorney (8675) Watanabe Kihei

5. Date of Amendment Order: Voluntary

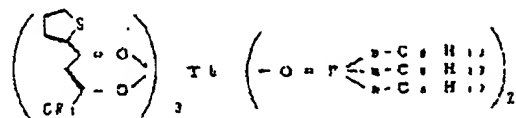
6. Object of Amendment: Specification

7. Content of Amendment:

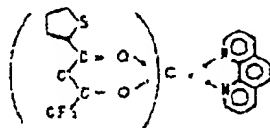
(1) In line 10, page 11 of the specification, amend "structural formula"



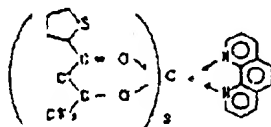
thus:



(2) In line 6, page 12 of the same, amend "structural formula"



thus:



(3) On pages 13-16 of the same, amend the whole text as on the separate sheet.

(4) In line 1, page 22 of the same, amend "2 x 10⁻⁴ moles" to "2 x 10⁻⁴ moles/l".

(5) In line 2, page 22 of the same, amend "5 x 10⁻⁴ moles" to "5 x 10⁻⁴ moles/l".

[formulac on page 9 to be inserted here]

Translator's Notes

1. Since Japanese seldom distinguishes between singular and plural, the translator into English has often to make context-based decisions as to which form to use. Hence, legal significance should not normally be attached to the use of singular or plural in translations from Japanese. A similar problem occurs in Claim 1, where A in MA₂ could be translated as "phosphine oxide", but the use of tri-n-octylphosphine oxide later in the text makes it clear that "a phosphine oxide" is correct here. Similarly, B in MB has been translated as "a phenanthroline", although only one phenanthroline is referred to in the text, so that "phenanthroline" may in fact have been meant.
2. Page 2, col. 1, line 8: "Vinsett" is just one possible transliteration for this name; the literature reference would of course provide the correct spelling.
3. Page 2, col. 1, line 9: "atracene" should perhaps be "anthracene".
4. Page 3, col. 1, line 29: "tribromomethyl" should perhaps be "tribromomethyl".
5. Page 3, col. 2, line 26: "gadolum" should perhaps be "gadolinium". In the same paragraph, the symbols for samarium and thulium were illegible, and have been assumed to be the standard Sm and Tm respectively.
6. The first paragraphs of Practical Examples 3, 4 and 5 seem to have omitted the use of TTA, NTFA and TTA respectively in the synthetic procedures concerned.
7. In the formal amendment (Page 8), the page numbers refer to the text blocks, four of which occur on each full page. Thus "page 11" means page 4, top left-hand block, and "page 12" means page 4, top right-hand block, and "pages 13-16" means the two blocks in the bottom half of page 4, plus the two blocks in the top half of page 5.